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Manganese Tricarbonyl Complexes with Asymmetric 2-Iminopyridine Ligands: Toward Decoupling Steric and Electronic Factors in Electrocatalytic CO₂ Reduction

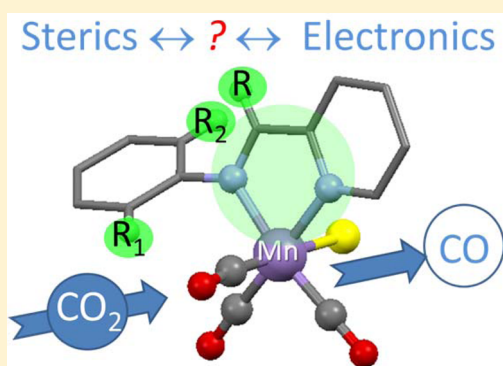
Steven J. P. Spall,[†] Theo Keane,[†] Joanne Tory,[‡] Dean C. Cocker,[†] Harry Adams,[†] Hannah Fowler,[†] Anthony J. H. M. Meijer,^{†,§} František Hartl,^{*,‡} and Julia A. Weinstein^{*,†,§}

[†]Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.

[‡]Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, U.K.

[§] Supporting Information

ABSTRACT: Manganese tricarbonyl bromide complexes incorporating IP (2-(phenylimino)pyridine) derivatives, [MnBr(CO)₃(IP)], are demonstrated as a new group of catalysts for CO₂ reduction, which represent the first example of utilization of (phenylimino)pyridine ligands on manganese centers for this purpose. The key feature is the asymmetric structure of the redox-noninnocent ligand that permits independent tuning of its steric and electronic properties. The α -diimine ligands and five new Mn(I) compounds have been synthesized, isolated in high yields, and fully characterized, including X-ray crystallography. Their electrochemical and electrocatalytic behavior was investigated using cyclic voltammetry and UV–vis–IR spectroelectrochemistry within an OTTE cell. Mechanistic investigations under an inert atmosphere have revealed differences in the nature of the reduction products as a function of steric bulk of the ligand. The direct ECE (electrochemical–chemical–electrochemical) formation of a five-coordinate anion [Mn(CO)₃(IP)][−], a product of two-electron reduction of the parent complex, is observed in the case of the bulky DIPIMP (2-(((2,6-diisopropylphenyl)imino)methyl)pyridine), TBIMP (2-(((2-*tert*-butylphenyl)imino)methyl)pyridine), and TBIEP (2-(((2-*tert*-butylphenyl)imino)ethyl)pyridine) derivatives. This process is replaced for the least sterically demanding IP ligand in [MnBr(CO)₃(IMP)] (2-[(phenylimino)methyl]pyridine) by the stepwise formation of such a monoanion via an ECEC(E) mechanism involving also the intermediate Mn–Mn dimer [Mn(CO)₃(IMP)]₂. The complex [MnBr(CO)₃(IPIMP)] (2-(((2-diisopropylphenyl)imino)methyl)pyridine), which carries a moderately electron donating, moderately bulky IP ligand, shows an intermediate behavior where both the five-coordinate anion and its dimeric precursor are jointly detected on the time scale of the spectroelectrochemical experiments. Under an atmosphere of CO₂ the studied complexes, except for the DIPIMP derivative, rapidly coordinate CO₂, forming stable bicarbonate intermediates, with no dimer being observed. Such behavior indicates that the CO₂ binding is outcompeting another pathway: viz., the dimerization reaction between the five-coordinate anion and the neutral parent complex. The bicarbonate intermediate species undergo reduction at more negative potentials (ca. −2.2 V vs Fc/Fc⁺), recovering [Mn(CO)₃(IP)][−] and triggering the catalytic production of CO.



The interest in solar fuels in terms of both photocatalytic and electrocatalytic CO₂ reduction,¹ in the latter case utilizing sustainable electricity, has been increasing markedly in the new millennium. The recent demonstration of the electrocatalytic activity of manganese² analogues of the archetypal Re(I) catalysts^{3–6} for CO₂ reduction has given a new impetus to research into noble-metal-free catalytic systems. [MnBr(CO)₃(α -diimine)] complexes have been shown to outperform rhenium-based analogues with regard to CO₂ reduction under certain conditions.⁷ Most notably, the presence of a Brønsted acid^{7–10} appears to be a prerequisite for catalysis with a range of tricarbonyl Mn α -diimine complexes.

Mechanistic studies^{5,10} of the active 2,2′-bipyridine-based (R-bpy) manganese catalysts have shown that one-electron reduction of the parent complex [MnBr(CO)₃(R-bpy)]

precursor results in the formation of the Mn–Mn dimer [Mn(CO)₃(R-bpy)]₂.^{8,9} Notably, neither the primary reduction product [MnBr(CO)₃(R-bpy)^{•−}] nor the five-coordinate radical intermediates [Mn(CO)₃(R-bpy)][•] have been detected by either UV–vis or IR spectroscopy.^{2,7} Nanosecond time-resolved infrared (TRIR) studies reveal that no detectable solvent adduct is formed before the dimerization of Mn species on this time scale; instead, the five-coordinate species is observed, which rapidly dimerizes.¹⁰ For some of the Re analogues, a one-electron-reduced complex, [ReCl(CO)₃(R-bpy)^{•−}], was observed by IR spectroscopy and identified by the ca. 15–20 cm^{−1} decrease in the $\tilde{\nu}(\text{CO})$ energy,^{11–13} as was the

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62 five-coordinate radical $[\text{Re}(\text{CO})_3(\text{tBu-bpy})]^\bullet$ by an additional
63 $15\text{--}20\text{ cm}^{-1}$ shift.

64 Two mechanisms have been proposed^{10,14–18} for the
65 ultimate reduction of $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})]_2$ in the presence
66 of CO_2 , which can be referred to as the anionic and the
67 oxidative addition¹⁹ pathways. The anionic pathway involves
68 reduction of the dimer $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})]_2$ at a potential
69 more negative than that of the parent complex, generating the
70 five-coordinate anion $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})]^-$, to which CO_2
71 coordinates and is catalytically reduced in the presence of a
72 Brønsted acid (the source of H^+). The anionic pathway is
73 broadly similar to the two-electron pathway observed for Re
74 complexes.^{20,21} In contrast, the uncommon second pathway
75 identified using pulsed EPR studies¹⁹ involves coordination of
76 CO_2 to the dimer $[\text{Mn}(\text{CO})_3(2,2'\text{-bpy})]_2$ in the presence of a
77 Brønsted acid in a concerted oxidative addition step. This
78 process is shown to generate a low-spin $\text{Mn}^{\text{II}}\text{--COOH}$ complex,
79 from which CO is subsequently released.

80 Since the catalytic CO_2 reduction with the use of
81 $[\text{MnX}(\text{CO})_3(\alpha\text{-diimine})]$ ($\alpha\text{-diimine} = \text{R-bpy}$; $\text{X} = \text{halide}$ or
82 pseudohalide) has been shown to proceed in many cases via a
83 dimerization step, immobilization of the catalyst²² or
84 introduction of sterically hindering groups at bpy may have a
85 profound effect on the catalytic activity.²³ Indeed, it has
86 recently been shown that the use of bipyridines incorporating
87 bulky groups in the 6,6'-positions^{24,25} (or another bulkier
88 heterocyclic ligand²⁶) largely inhibits dimerization in the
89 catalytic cycle. The result is the formation of the stable five-
90 coordinate anion via the two-electron transfer (ECE) at the first
91 cathodic wave. However, coordination of CO_2 to the five-
92 coordinate anion produces a stable species which must be
93 reduced at considerably more negative potentials²⁷ in order for
94 catalysis to be observed. It has recently been shown that in the
95 presence of a Lewis acid, Mg^{2+} ,^{7,28} the catalytic overpotential²⁹
96 is decreased by approximately 400 mV.

97 A similar behavior was observed for $[\text{MnBr}(\text{CO})_3(\text{R-DAB})]$
98 complexes featuring nonaromatic 1,4-diazabuta-1,3-diene (R-
99 DAB)^{8,9,30} ligands. The reduction potentials of the dimers
100 $[\text{Mn}(\text{CO})_3(\text{R-DAB})]_2$ are almost identical with those of the
101 parent complexes, implying that the five-coordinate anion is
102 produced directly upon reduction and reacts readily with CO_2
103 in solution to form a stable bicarbonate complex^{8,30} and, as
104 with sterically hindered 2,2'-bipyridine ligands,²⁵ a much more
105 negative potential (below 2 V vs Fc/Fc^+) must be applied to
106 trigger catalytic CO_2 reduction. Functionalization of the α -
107 diimine with a sterically bulky group such as tBu should also
108 modify the electronic properties of the ligand. In particular, this
109 change should affect the energy of the LUMO, the reduction
110 potential, and catalytic activity.^{23–33}

111 Introducing steric bulk^{23,25} to prevent unwanted reactions of
112 the catalytic species, including dimerization as either Mn--Mn ⁹
113 or $\text{C(imino)--C(imino)}$ bound species,²¹ while at the same
114 time reducing the risk of increased overpotential is a
115 challenging task. Molecular designs that allow for steric and
116 electronic effects to be decoupled are required.

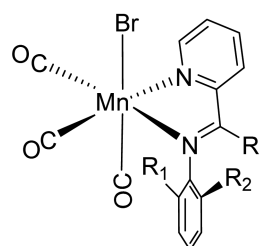
117 In this paper we have investigated a family of tricarbonyl
118 manganese complexes featuring asymmetric α -diimine ligands,
119 iminopyridines (IP).^{21,23,34,35} They combine an accessible
120 --C=N-- imino bond of the diazabuta-1,3-diene derivatives
121 DAB³² with the aromatic pyridine part, thereby being a
122 “hybrid” of 2,2'-bipyridine ligands and nonaromatic R-DAB
123 ligands. Each of the parts is important: for instance, a $\text{Mn}(\text{I})$
124 complex with Ph-DAB demonstrates formation of five-

coordinate anions, with the steric bulk of the ligand preventing
dimerization, but does not act as a catalyst for CO_2 reduction
due to insufficiently negative reduction potential.⁸

Introduction of the pyridine moiety allows one to reach the
required reduction potentials, while the Ph group attached to
the C=N fragment can be decorated with sterically demanding
substituents, ensuring steric bulk while only slightly affecting
the electronic properties. As the phenyl moiety lies out of plane
with the conjugated α -diimine (because of steric effects), the π
electrons of the phenyl substituent are decoupled from the
metallacycle formed by the metal center and the α -diimine.
Therefore, functionalization of the phenyl ring in the R_1 and R_2
positions with large sterically hindering groups (that also have a
+I effect) will have only very minimal effects on the electronics
of the active site of the molecule (vide infra). These ligands
offer an opportunity to separate steric and electronic effects in a
chelating α -diimine ligand to a certain extent. Thus, the
possibility arises of a systematic variation of the steric hindrance
by changing R_1 and R_2 groups, while the R group strongly
influences the electronics (but could also hinder the C=N
bond).

These ligands are readily accessible via simple synthetic
routes, which are suitable for the purpose of comparatively
independent alteration of steric and electronic effects (Chart 1).

Chart 1. General Structure of the Complexes with the Asymmetric α -Diimine Ligands (2- R_1 -6- R_2 -phenyl)(R -imino)pyridine^a



Ligand	R	R_1	R_2
IMP (1)	H	H	H
IPIMP (2)	H	tPr	H
DIPIMP (3)	H	tPr	tPr
TBIMP (4)	H	tBu	H
TBIEP (5)	CH_3	tBu	H

^aNumbers given in parentheses correspond to the Mn complexes. When $\text{R} = \text{H}$, the ligands will be derivatives of [(phenylimino)methyl]pyridine: IMP ($\text{R}_{1,2} = \text{H}$), IPIMP ($\text{R}_1 = \text{tPr}$, $\text{R}_2 = \text{H}$), and DIPIMP ($\text{R}_{1,2} = \text{tPr}$), TBIMP ($\text{R}_1 = \text{tBu}$, $\text{R}_2 = \text{H}$). $\text{R} = \text{CH}_3$ gives TBIEP, [((*tert*-butylphenyl)imino)ethyl]pyridine.

The potential of such ligands^{34–38} has been convincingly
illustrated by the recent work on a Re tricarbonyl complex with
2-[[((2-cyclohexyl-1-methyl)methyl)imino]pyridine³⁶ (both the
one-electron-reduced parent complex and the neutral five-
coordinate $\text{Re}(\text{I})$ species were detected), and Mo pyridine-
monoimides.³⁴

Herein we report a new series of manganese-based catalysts
for CO_2 reduction. We will show that a change in the structure
of the ligands within the same series affects the efficiency of the
process and the relative distribution of the intermediate species,
demonstrating the versatile and tunable nature of these types of
catalysts.

EXPERIMENTAL SECTION

All solvents were supplied by VWR and used as received. The
compounds were purchased from either Sigma-Aldrich or Strem
Chemicals and, unless stated, used as received. Tetrabutylammonium
hexafluorophosphate, $[\text{Bu}_4\text{N}][\text{PF}_6]$, was recrystallized from hot
ethanol and dried overnight in a vacuum oven before use in the
electrochemical studies. TBIEP (2-[[((2-*tert*-butylphenyl)imino)ethyl]-

pyridine) and TBIMP were synthesized as previously described;³⁵ the analytical data matched those reported previously. Unless otherwise stated, UV–vis spectra were recorded on a Carry 50 Bio spectrophotometer and IR spectra on a PerkinElmer Spectrum 1 FT-IR spectrometer.

Syntheses. *IMP* (2-[(Phenylimino)methyl]pyridine). Aniline (11.3 mmol, 1.05 g, 1.02 mL) was added to 2-pyridinecarboxaldehyde (11.3 mmol, 1.2 g, 1.1 mL) in flame-dried glassware and stirred for 1 h. Hexane (10 mL) was added and the solution dried over sodium sulfate. The solution was filtered, concentrated under vacuum, and placed in a freezer overnight. The large yellow needlelike crystals that formed were filtered and washed with hexane. Yield: 73%. ¹H NMR (400 MHz, CDCl₃): δ 8.72 (d, *J* = 4.7 Hz, 1H), 8.61 (s, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 7.83 (td, *J* = 7.7, 1.6 Hz, 1H), 7.47–7.35 (m, 3H), 7.29 (d, *J* = 7.7 Hz, 3H), 1.58 (s, 4H).

IPIMP (2-[2-[(Isopropylphenyl)imino)methyl]pyridine). 2-Isopropylaniline (12.4 mmol, 1.7 g, 1.8 mL) was mixed with 2-pyridinecarboxaldehyde (12.4 mmol, 1.3 g, 1.2 mL) in flame-dried glassware and stirred for 1 h. Hexane (20 mL) was added and the solution dried over sodium sulfate. The solution was filtered and solvent removed under vacuum, yielding the product as a brown oil. Previous reports indicated that this compound could not be crystallized; therefore, the oil was used in the next reaction step without further purification (purity by NMR >97%). ¹H NMR (400 MHz, CDCl₃): δ 8.72 (ddd, *J* = 4.8, 1.6, 0.9 Hz, 1H), 8.54 (s, 1H), 8.26 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.82 (ddd, *J* = 7.9, 1.7, 0.8 Hz, 1H), 7.45–7.32 (m, 2H), 7.31–7.22 (m, 2H), 7.08–6.96 (m, 1H), 3.56 (dp, *J* = 13.8, 6.8 Hz, 1H), 1.26 (dd, *J* = 6.8, 4.1 Hz, 7H).

DIPIMP (2-[(2,6-Diisopropylphenyl)imino)methyl]pyridine). 2,6-Diisopropylaniline (11.3 mmol, 2 g, 2.1 mL) was mixed with 2-pyridinecarboxaldehyde (11.3 mmol, 1.2 g, 1.1 mL) in flame-dried glassware and stirred for 2 h. Hexane (10 mL) was added and the solution dried over sodium sulfate. The solution was filtered and concentrated before being placed in a freezer overnight. Light brown to yellow crystals were formed, which were filtered off and washed with hexane. Yield: 67%. ¹H NMR (400 MHz, CDCl₃): δ 8.73 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.31 (s, 1H), 8.27 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.90–7.82 (m, 1H), 7.42 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 7.22–7.07 (m, 3H), 2.97 (hept, *J* = 6.9 Hz, 2H), 1.62 (s, 1H), 1.18 (d, *J* = 6.9 Hz, 13H).

Complexes 1–6 were prepared from [MnBr(CO)₅] and the corresponding ligand, using diethyl ether as a solvent. The products were collected by centrifugation and washed with diethyl ether to afford analytically pure 1–6. ¹H NMR spectra for 1–5 are given in Figure S122–S126 in the Supporting Information.

[MnBr(CO)₅(IMP)] (1). [MnBr(CO)₅] (1.1 mmol, 0.3 g) was combined with IMP (1.1 mmol, 0.2 g) in diethyl ether (20 mL) and refluxed under aerobic conditions for 4 h.³⁹ The product was formed in quantitative yield. ¹H NMR (500 MHz, CDCl₃): δ 9.26 (d, *J* = 5.0 Hz, 1H), 8.45 (s, *J* = 27.9 Hz, 1H), 8.14–7.79 (m, 3H), 7.68–7.36 (m, 5H). HRMS (TOF-ES, +ve): *m/z* (M + Na⁺) calcd for C₁₅H₁₀N₂O₃NaBrMn 422.9153, found 422.9149.

[MnBr(CO)₅(IPIMP)] (2). [MnBr(CO)₅] (0.89 mmol, 0.24 g) was combined with IPIMP (0.89 mmol, 0.2 g) in diethyl ether (20 mL) and refluxed under aerobic conditions for 4 h. The product was formed in quantitative yield. ¹H NMR (500 MHz, CDCl₃): δ 9.27 (s, 1H), 8.39 (s, 1H), 8.04 (s, 1H), 7.94 (d, *J* = 4.1 Hz, 1H), 7.78 (d, *J* = 7.0 Hz, 1H), 7.61 (s, 1H), 7.48 (d, *J* = 15.3 Hz, 1H), 7.43 (d, *J* = 6.7 Hz, 1H), 7.37 (t, 1H), 7.30 (d, *J* = 6.9 Hz, 1H), 3.58 (s, 1H), 3.03 (d, *J* = 35.6 Hz, 1H), 1.47–1.11 (m, 1H). HRMS (TOF-ES, +ve): *m/z* (M + Na⁺) calcd for C₁₈H₁₆N₂O₃NaBrMn 464.9622, found 464.9644.

[MnBr(CO)₅(DIPIMP)] (3). [MnBr(CO)₅] (0.75 mmol, 0.2 g) was combined with DIPIMP (0.75 mmol, 0.2 g) in diethyl ether (20 mL) and refluxed under aerobic conditions for 4 h. The product was formed in 97% yield. ¹H NMR (500 MHz, CDCl₃): δ 9.30 (s, 1H), 8.41 (s, 1H), 7.99 (d, *J* = 50.7 Hz, 2H), 7.63 (s, 1H), 7.34 (s, 2H), 4.04 (s, 1H), 2.91 (s, 1H), 1.34 (d, *J* = 3.1 Hz, 6H), 1.05 (dd, *J* = 80.6, 35.1 Hz, 6H). HRMS (TOF-ES, +ve): *m/z* (M + Na⁺) calcd for C₂₁H₂₂N₂O₃NaBrMn 507.0092, found 507.0107.

[MnBr(CO)₅(TBIMP)] (4). [MnBr(CO)₅] (0.84 mmol, 0.23 g) was combined with DIPIMP (0.84 mmol, 0.2 g) in diethyl ether (20 mL) and refluxed under aerobic conditions for 4 h. The product was formed in quantitative yield. ¹H NMR (400 MHz, CDCl₃): δ 9.27 (d, *J* = 4.4 Hz, 1H), 8.50 (s, 1H), 8.12 (d, *J* = 6.9 Hz, 1H), 8.03 (t, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 7.1 Hz, 1H), 7.61 (t, *J* = 6.2 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.30 (t, 1H), 1.43 (s, 1H). HRMS (TOF-ESI, +ve): *m/z* (M + Na⁺) calcd for C₁₉H₁₈N₂O₃NaBrMn 478.9774, found 478.9789.

[MnBr(CO)₅(TBIEP)] (5). [MnBr(CO)₅] (0.8 mmol, 0.22 g) was combined with TBIEP (0.8 mmol, 0.2 g) and refluxed under aerobic conditions in diethyl ether (20 mL) for 4 h. The product was formed in quantitative yield. ¹H NMR (400 MHz, CDCl₃): δ 9.28 (d, *J* = 5.0 Hz, 1H), 8.04 (td, *J* = 7.8, 1.3 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.88 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.65–7.54 (m, 2H), 7.34–7.27 (m, 2H), 2.39 (s, 3H), 1.39 (s, 8H). HRMS (TOF-ES, +ve): *m/z* (M + Na⁺) calcd for C₂₀H₂₀N₂O₃NaBrMn 492.9935, found 492.9934.

[MnBr(CO)₅(bpy)] (6). This compound was prepared following the literature procedure;² analytical data are in agreement with the literature data. [MnBr(CO)₅] (1.28 mmol, 0.35 g) was combined with 2,2′-bipyridine (1.28 mmol, 0.2 g) in diethyl ether (20 mL) and refluxed under aerobic conditions for 4 h. The product was formed in 80% yield. ¹H NMR (500 MHz, CDCl₃): δ 9.27 (d, *J* = 4.3 Hz, 1H), 8.12 (d, *J* = 6.5 Hz, 1H), 7.99 (t, 1H), 7.53 (t, 1H). HRMS (TOF-ESI, +ve): *m/z* (M + Na⁺) calcd for C₁₃H₈N₂O₃NaBrMn 396.8991, found 369.8988.

Cyclic Voltammetry. Cyclic voltammetry was performed using a Princeton Applied Research VersaSTAT3 potentiostat on 2 mM 1–6 in Grubbs dried HPLC-grade acetonitrile containing 2 × 10^{−1} M [Bu₄N][PF₆] as supporting electrolyte. A glassy-carbon working electrode (surface area 0.07 cm², polished on alumina and paper) and a Pt-wire counter electrode were used with a 0.1 M KCl Ag/AgCl reference electrode.

The solutions were deoxygenated by bubbling thoroughly with bottled N₂ (BOC), and the N₂ atmosphere was maintained over the samples during the experiment. To test for catalytic current in the presence of CO₂, the samples were bubbled thoroughly with bottled CO₂ (BOC) and cyclic voltammograms (CVs) were recorded under an atmosphere of CO₂ (some residual water might be present in the CO₂ used to saturate the samples). Water was then added (0.3–6 mL of the solution of each sample) to test the effects of Brønsted acid. Ferrocene was added as the internal standard at the end of all experiments.

Spectroelectrochemistry. Infrared spectroelectrochemistry was performed using an EmStat3 or EmStat3+ potentiostat (PalmSens, Houten, The Netherlands). The solution of 4 mM complex in the presence of 3 × 10^{−1} M [Bu₄N][PF₆] in dry acetonitrile was analyzed using an optically transparent thin-layer electrochemical (OTTLE) cell equipped with Pt minigrid working and auxiliary electrodes, an Ag-microwire pseudoreference electrode, and CaF₂ windows. Samples were prepared under an argon atmosphere; for electrocatalytic measurements, the solutions were bubbled with CO₂ on a frit (a few minutes) to saturation under normal pressure. Parallel IR and UV–vis spectral monitoring during the spectroelectrochemical experiment was performed on a Bruker Vertex 70v FT-IR spectrometer or PerkinElmer Spectrum 1 and a Scinco S-3100 spectrophotometer, respectively. Thin-layer CVs were recorded in the course of the experiment.

Gas Chromatography Linked to Electrolysis. Bulk electrolysis was performed on a 0.17 mM solution of each of the complexes in a 60 mL solution of acetonitrile/water (9/1 v/v). The cell setup consisted of a Pt-mesh working electrode, a Pt-rod counter electrode in a semiporous compartment, and an Ag-wire pseudoreference electrode in a 0.1 M KCl solution. The potential of the Fc/Fc⁺ recorded in this setup using a glassy-carbon 3 mm diameter electrode was +0.350 V vs Ag wire pseudoreference. Hence, in order to reach the potential necessary for the CO₂ reduction as estimated from the CV data, the potential was held at −1.9 V vs Ag wire for all samples: i.e., −2.25 V vs Fc/Fc⁺. Prior to electrolysis, a CV was recorded in the bulk electrolysis cell using a glassy-carbon working electrode. Gas samples (100 μL) were withdrawn from the head space at regular intervals and analyzed

by a gas chromatograph fitted with a thermal conductivity detector (Perkin Elmer Autosystem XL). H₂ was used as the carrier gas in CO-quantification experiments. N₂ was used as a carrier gas in the control experiment.

X-ray Crystallography. Crystals were grown using the antisolvent crystallization method, with the solvent dichloromethane and hexane as the antisolvent. Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX-II CCD diffractometer operating a Mo K α sealed-tube X-ray source or a Bruker D8 Venture diffractometer equipped with a PHOTON 100 dual-CMOS chip detector and operating a Cu K α I μ S microfocus X-ray source. The data were processed using Bruker APEX3 software and corrected for absorption using empirical methods (SADABS) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.⁴⁰ The crystal structures were solved and refined using the Bruker SHELXTL software package.

Computational Methods. Density functional theory (DFT) calculations were performed using the Gaussian 09 program package.⁴¹ All calculations utilized the global hybrid exchange correlation functional B3LYP,^{42,43} a “mixed” basis set consisting of the SDD basis set as defined in Gaussian for Mn and the 6-311G(d,p) basis set for all other atoms.^{44–47} The solvent acetonitrile was included using the polarizable continuum model (PCM) as implemented in Gaussian.^{48,49} All species were modeled at the lowest multiplicity appropriate for the electron count, and the restricted formalism was used for closed-shell cases. An “ultrafine” integral grid, as defined by Gaussian, was used and all geometries were confirmed as minima by the absence of imaginary frequencies in their vibrational spectra as calculated within the harmonic approximation. The values of vibrational frequencies have been scaled by 0.966 to match experimental $\nu(\text{CO})$ values of the parent neutral complexes.

RESULTS AND DISCUSSION

X-ray Crystallography. The crystal structures of the complexes [MnBr(CO)₃(α -diimine)] (α -diimine = TBIEP, IMP, IPIMP, DIPIMP) are shown in Figure 1, and selected bond distances and angles are given in Table S11 in the Supporting Information. Similar bond lengths are observed for the four complexes, and these are in good agreement with related [MnBr(CO)₃(α -diimine)] species reported in the literature. The X-ray data are in good agreement with the results obtained through DFT calculations. As predicted by

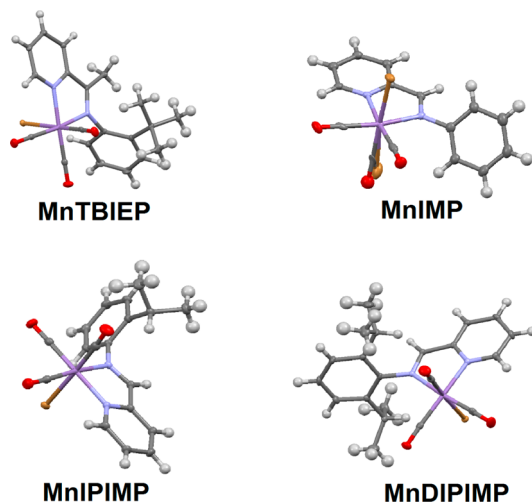


Figure 1. X-ray crystal structures of the studied complexes shown with thermal ellipsoids at the 50% probability level. CCDC 1457930 (MnTBIEP), 1457931 (MnDIPIMP), 1457932 (MnIPIMP), 1457933 (MnIMP). Full crystallographic details are given in the Supporting Information.

DFT, the pyridine and phenyl rings lie approximately orthogonally to one another (dihedral angles between the corresponding planes are MnTBIEP 84.55°, MnIPIMP 83.64°, MnDIPIMP 78°), resulting in little orbital overlap between these two moieties, with the exception of MnIMP, where the two ring systems were significantly less orthogonal (56.54°).

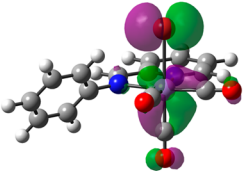
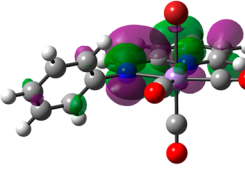
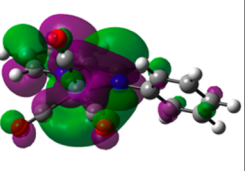
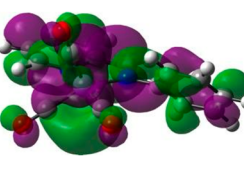
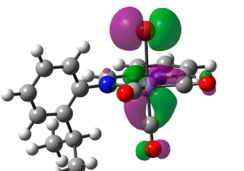
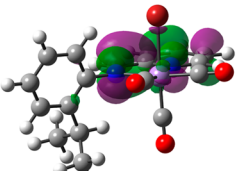
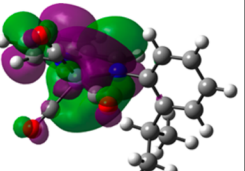
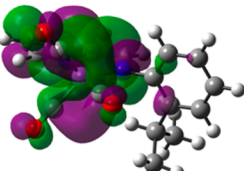
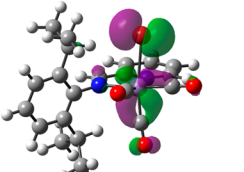
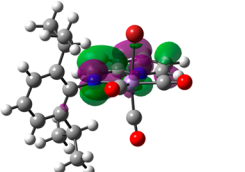
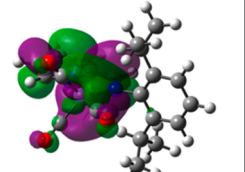
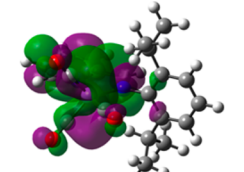
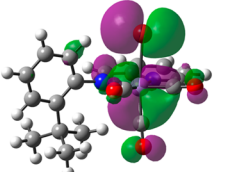
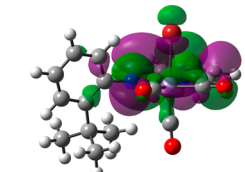
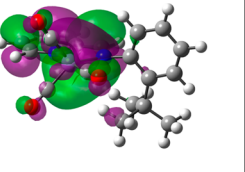
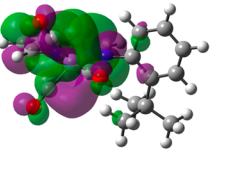
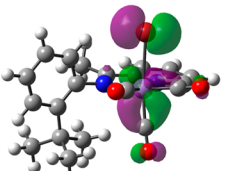
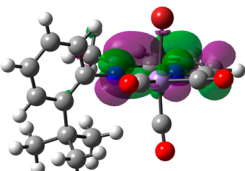
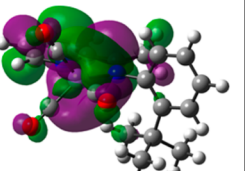
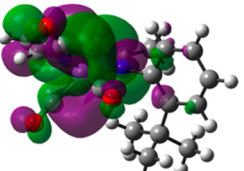
The crystal structures have revealed significant steric hindrance between the substituents R = Me and R₁ = ^tBu in MnTBIEP, which inhibits rotation of the Ph ring and confers conformational rigidity. Rotation of the Ph ring in MnDIPIMP is also inhibited by the two ⁱPr groups and hence also has conformational rigidity. In contrast, MnIMP and MnIPIMP exhibit much smaller steric hindrance, facilitating the rotation of the phenyl ring.

Computational Investigations of Molecular Structures and Frontier Orbitals by DFT. The optimized geometries of the studied complexes with frontier orbitals overlaid as calculated by DFT are displayed in Table 1. As anticipated, the phenyl group lies out of the plane of the chelating diimine. The HOMO is localized predominantly over the axial Br–Mn–C(O) bonds with almost no contribution from the phenyl moiety. The LUMO resides largely on the imine, pyridyl, and metal center, with minimal contribution from the C1–C2 and C1–C6 σ bonds of the phenyl groups. In the case of MnIMP, due to the lack of substitution at R₁ and R₂, the phenyl moiety is less sterically hindered and thus is positioned closer to the plane of the imino-pyridine fragment, resulting in a small degree of involvement of the phenyl π system in the low-energy unoccupied orbitals. This trend continues in the other low-energy unoccupied orbitals (see Figures S11–S110 in the Supporting Information).

The energies of the HOMO in all complexes are within 0.02 eV of each other, and all compounds in the IMP subset of complexes have a LUMO that lies within 0.03 eV of those of the other complexes. In contrast, MnTBIEP shows a difference in LUMO energy of +0.19 eV in comparison with IPIMP. This larger difference in LUMO energy comes as result of methylation at the R position. In contrast, adding two isopropyl groups at the R₁ and R₂ positions resulted in an energy difference of just 0.02 eV between MnIMP and MnDIPIMP. The results of the calculations on the trends in the energies of HOMO/LUMO are in full agreement with the experimentally determined redox potentials (see below). These results imply that an almost complete separation between the steric and the electronic effects in the context of few-electron reductions can indeed be achieved in this series of complexes. Changing the R group will strongly affect the energy of the LUMO while also having some impact on the steric properties at the carbon of the imino C=N bond, while changing the R₁ or R₂ groups should have considerable effects on the steric hindrance of the molecule (protecting the Mn and imino-N centers) but hardly affect its electronic properties.

The experimental and calculated carbonyl vibrational frequencies of the studied complexes are shown in Table 2. The calculated frequencies are in good agreement with the experimental values. Some systematic discrepancies are apparent: the high-energy A'(1) mode tends to be underestimated by $\sim 10\text{ cm}^{-1}$, the A'' mode tends to have a lower deviation of only $\sim 2\text{ cm}^{-1}$, and the low-energy A'(2) mode tends to be overestimated by $\sim 10\text{ cm}^{-1}$. It is clear that attachment of the methyl group as R increases the electron density on the metal center and thus also the Mn to CO π back-bonding, as evidenced by the smaller values of $\nu(\text{CO})$ for

Table 1. Frontier Orbitals of the Complexes 1–5 and the Corresponding Five-Coordinate Anions Calculated at the B3LYP/SDD+6-311G(d,p)/IEFPCM Level^a

HOMO	LUMO	HOMO	LUMO
Parent Complex		Five-coordinate anion	
MnIMP		MnIMP	
			
$\epsilon = -6.31 \text{ eV}$	$\epsilon = -2.84 \text{ eV}$	$\epsilon = -3.67 \text{ eV}$	$\epsilon = -1.18 \text{ eV}$
MnIPIMP		MnIPIMP	
			
$\epsilon = -6.33 \text{ eV}$	$\epsilon = -2.81 \text{ eV}$	$\epsilon = -3.70 \text{ eV}$	$\epsilon = -1.01 \text{ eV}$
MnDIPIMP		MnDIPIMP	
			
$\epsilon = -6.31 \text{ eV}$	$\epsilon = -2.83 \text{ eV}$	$\epsilon = -3.67 \text{ eV}$	$\epsilon = -0.99 \text{ eV}$
MnTBIMP		MnTBIMP	
			
$\epsilon = -6.36 \text{ eV}$	$\epsilon = -2.80 \text{ eV}$	$\epsilon = -3.64 \text{ eV}$	$\epsilon = -1.02 \text{ eV}$
MnTBIEP		MnTBIEP	
			

^aIsovalue of 0.04 ($e \text{ bohr}^{-3}$)^{1/2}.

MnTBIEP in comparison to the IMP subseries (complexes 1–4). However, substitution at R₁ and R₂ has only a slight effect on the frequencies. It should be noted that the magnitude of these effects is small ($<10 \text{ cm}^{-1}$) and that it is beyond the scope of this computational work to unravel the various factors effecting changes in CO stretching frequencies.⁵⁰ The results of DFT calculations (Table 2) of IR spectra for the parent Br complexes [MnBr(CO)₃(α -diimine)] (1–5) and the corresponding [Mn(CO)₃(H₂O)(α -diimine)]⁺ (cationic

aquo complexes) match the experimental data well. We therefore use the calculated $\nu(\text{CO})$ wavenumbers for the hydrolyzed aquo and reduced (dimer and anion) species to aid the analysis of the IR spectra and product assignment in the course of the corresponding cathodic IR-SEC experiments (vide infra).

Adding electron-donating groups ('Pr, 'Bu) to the phenyl ring of the IMP subseries does not have a large effect on the $\nu(\text{CO})$ frequency, the band positions being virtually unchanged

Table 2. Experimentally Obtained and Calculated Frequencies of Carbonyl Stretching Vibrations, $\nu(\text{CO})$, of the Mn Complexes in Their Neutral Form (1–5) and Transient One-Electron-Reduced Form, as well as Five-Coordinate Anion, a Cationic Aqua Complex, and an Mn–Mn Bound Dimer^a

species	$\nu(\text{CO})/\text{cm}^{-1}$	
	calcd	exptl
[MnBr(CO) ₃ (IMP)] (1)	2020, 1943, 1931	2029, 1941, 1926
[MnBr(CO) ₃ (IMP)] [−]	1992, 1906, 1897	not obsd
[Mn(CO) ₃ (H ₂ O)(IMP)] ⁺	2046, 1966, 1957	2051, 1964, 1958 ^b
[Mn(CO) ₃ (IMP)] [−]	1906, 1830, 1813	1930, 1826
[Mn(CO) ₃ (IMP)] ₂	1964, 1918, 1891, 1882, 1872, 1868	1994, 1949, 1902, 1875
[MnBr(CO) ₃ (IPIMP)] (2)	2020, 1945, 1929	2029, 1943, 1923
[MnBr(CO) ₃ (IPIMP)] [−]	1988, 1905, 1891	not obsd
[Mn(CO) ₃ (H ₂ O)(IPIMP)] ⁺	2044, 1963, 1956	2049, 1959 (br)
[Mn(CO) ₃ (IPIMP)] [−]	1905, 1826, 1808	1929, 1824
[Mn(CO) ₃ (IPIMP)] ₂	1964, 1917, 1890, 1881, 1866, 1860	1981, 1949, 1901, 1882, 1862
[MnBr(CO) ₃ (DIPIMP)] (3)	2019, 1945, 1929	2028, 1944, 1922
[MnBr(CO) ₃ (DIPIMP)] [−]	1985, 1906, 1890	not obsd
[Mn(CO) ₃ (H ₂ O)(DIPIMP)] ⁺	2045, 1964, 1957	2050, 1960 (br) ^b
[Mn(CO) ₃ (DIPIMP)] [−]	1903, 1824, 1806	1929, 1829/1822
[Mn(CO) ₃ (DIPIMP)] ₂	1965, 1918, 1890, 1880, 1860, 1850	not obsd
[MnBr(CO) ₃ (TBIMP)] (4)	2020, 1947, 1925	2029, 1945, 1923
[MnBr(CO) ₃ (TBIMP)] [−]	1988, 1907, 1890	not obsd
[Mn(CO) ₃ (H ₂ O)(TBIMP)] ⁺	2045, 1965, 1956	not obsd
[Mn(CO) ₃ (TBIMP)] [−]	1906, 1827, 1807	1928, 1823
[Mn(CO) ₃ (TBIMP)] ₂	1964, 1916, 1889, 1879, 1862, 1854	not obsd
[MnBr(CO) ₃ (TBIEP)] (5)	2018, 1944, 1921	2028, 1943, 1917
[MnBr(CO) ₃ (TBIEP)] [−]	1980, 1904, 1883	not obsd
[Mn(CO) ₃ (H ₂ O)(TBIEP)] ⁺	2042, 1962, 1950	2048, 1960, 1954
[Mn(CO) ₃ (TBIEP)] [−]	1897, 1819, 1798	1922, 1814 (br)
[Mn(CO) ₃ (TBIEP)] ₂	1958, 1909, 1880, 1870, 1850, 1841	not obsd

^aIn acetonitrile at 293 K. ^bPositions are approximate, as the parent CO stretching vibrations obscure those of the cationic aqua complex.

The UV–vis absorption spectra (Figure 2) are consistent with the nature of the frontier orbitals obtained from the

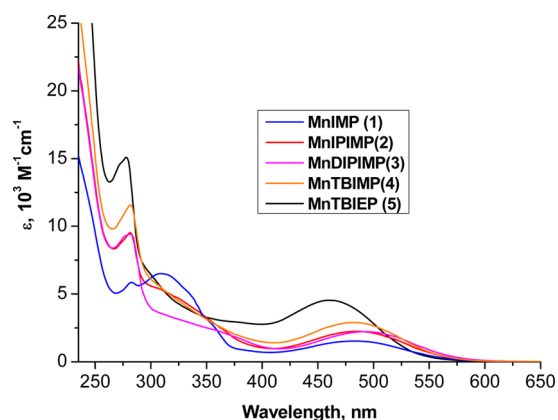


Figure 2. Electronic absorption spectra of the manganese complexes 1–5 studied in this work, in DCM at 293 K.

calculated data. The lowest energy absorption band for the complexes of the IMP subseries 1–4 occurs at approximately the same ca. 500 nm position. In contrast MnTBIEP (5) exhibits an absorption band with a maximum at a shorter wavelength, 460 nm, due to electron donation from the Me group which destabilizes the LUMO.

Cyclic Voltammetry. Electrochemical studies showed significant differences between the cathodic path of MnTBIEP (5) and those of the IMP subseries (1–4).

Under an N₂ atmosphere, [MnBr(CO)₃(TBIEP)] shows a single reduction wave at $E_{p,c} = -1.53$ V and an intense anodic wave at $E_{p,a} = -1.3$ V observed on the reverse anodic scan. This behavior is similar to that of [MnBr(CO)₃(Pr-DAB)] (Pr-DAB = 1,4-diisopropyl-1,4-diazabuta-1,3-diene),⁸ which is reduced by an ECE mechanism. The initial one-electron reduction results in dissociation of the bromide to form a five-coordinate radical, [Mn(CO)₃(TBIEP)][•], which is concomitantly reduced to the five-coordinate anion [Mn(CO)₃(TBIEP)][−] (reoxidized at −1.3 V) at the potential required for the reduction of [MnBr(CO)₃(TBIEP)]. A small anodic wave at −0.6 V is characteristic of oxidation of [Mn(CO)₃(TBIEP)]₂ formed in the course of the anodic path of the five-coordinate anion, and indicates that dimerization can still occur with R = CH₃. The dimer could also be produced in a reaction of [Mn(CO)₃(TBIEP)][−] with neutral [MnBr(CO)₃(TBIEP)] on the cathodic scan, but the absence of a cathodic wave for reduction of [Mn(CO)₃(TBIEP)]₂ indicates that its reduction potential is too close to that of [MnBr(CO)₃(TBIEP)] for a separate reduction wave to be observed.

The CV traces of MnIMP obtained under a N₂ atmosphere show three cathodic reduction peaks at $E_{p,c} = -1.28$, −1.41, and −1.54 V and a strong anodic peak at $E_{p,a} = -1.24$ V. The first reduction at −1.28 V can be assigned to the cation [Mn(CO)₃(H₂O)(IMP)]⁺; it is likely that the peak at −1.41 V is due to remaining nonhydrolyzed [MnBr(CO)₃(IMP)] or a solvent adduct,¹¹ while the −1.54 V wave corresponds to the reduction of the dimeric species (see also the IR spectroelectrochemical section below). The five-coordinate anion [Mn(CO)₃(IMP)][−] is probably the reduction product at all three different cathodic waves (the parent complex [MnBr(CO)₃(IMP)], aquo complex, and the IMPMn–MnIMP

among complexes 1–4. The two higher-frequency bands are at 2028–2029 and 1943–1944 cm^{−1} for all five complexes, while the lowest $\nu(\text{CO})$ band is seen at 1923–1922 cm^{−1} for the IMP series but is shifted to lower energy, 1917 cm^{−1} in [MnBr(CO)₃(TBIEP)], where the increased π back-donation is caused by R = Me. This invariability of $\nu(\text{CO})$ frequencies, while the dihedral angles between the planes of the pyridine and phenyl moieties of the IP ligands are clearly changing drastically, from ~56 to ~84°, confirms the opportunity of the somewhat independent tuning of electronic and steric factors. Calculations performed on the five-coordinate anions of the studied compounds, [Mn(CO)₃(diimine)][−], show trends very similar to what has been observed in the parent complexes. Both the HOMO and LUMO are predominantly delocalized over the tricarbonyl-Mn and α -diimine metallacycle, with little participation from the phenyl ring, with the exception of MnIMP, the LUMO of which has a significant contribution from the phenyl moiety.

dimer), as evidenced by its anodic wave at $E_{p,a} = -1.24$ V on the reverse anodic scan (accompanied by the dimer oxidation above -0.5 V).

Over time a smaller cathodic wave emerges at $E_{p,c} -1.35$ V, due to the aquo-coordinated cationic complex forming via hydrolysis of the parent Br complex (see Figures S111 and S112 in the Supporting Information). Under an atmosphere of CO_2 the anodic wave of $[\text{Mn}(\text{CO})_3(\text{TBIEP})]^-$ at -1.3 V disappears, and the profile of the CV also changes (Figure 3), with a broad

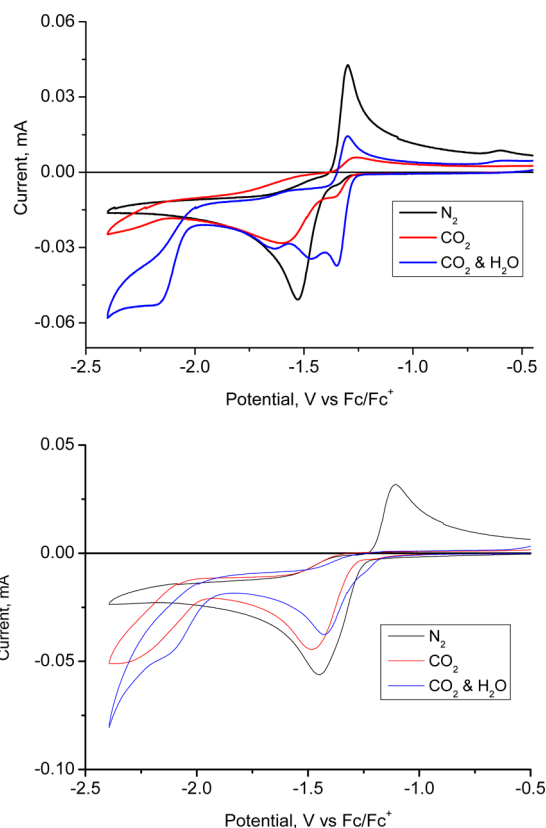


Figure 3. Cyclic voltammograms of 1 mM MnTBIEP (top panel) and MnTBIMP (bottom panel) in acetonitrile with 0.2 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte, under a N_2 atmosphere (black), CO_2 atmosphere (red), and CO_2 with 4.7% added water (blue) at a scan rate of 0.1 V s^{-1} .

cathodic wave of $[\text{MnBr}(\text{CO})_3(\text{TBIEP})]$ shifted slightly negatively, indicating an interaction with CO_2 . However, similar to the case for Mn-bpy complexes,² catalytic reduction of CO_2 in the absence of a Brønsted acid was not observed (the small peak beginning around -2.18 V is due to a small amount of water entering the CV cell when it is being saturated with CO_2). Addition of 0.3 mL of water leads to significant current enhancement at -2.18 V, in line with what has been observed with $[\text{MnBr}(\text{CO})_3(\text{iPr-DAB})]$.⁸

Under a CO_2 atmosphere, the increased cathodic current is seen at ~ -2.2 V for all complexes. We believe this is due to some amount of the bicarbonate complex being formed, likely due to traces of water in the CO_2 used.³³ When 10% water is added to the CO_2 -saturated solution, a strong current enhancement is observed at -2.21 V. Importantly, CVs recorded under a N_2 atmosphere in acetonitrile in the presence of water do not show catalytic current enhancement (see Figures S114–S118 in the Supporting Information); thus, both

CO_2 and water are required for the current enhancement to be observed.

Under a CO_2 atmosphere, no anodic wave corresponding to reoxidation of the five-coordinate anion is observed for the least sterically hindered $[\text{Mn}(\text{CO})_3(\text{IMP})]^-$ (Figure 4) or for the

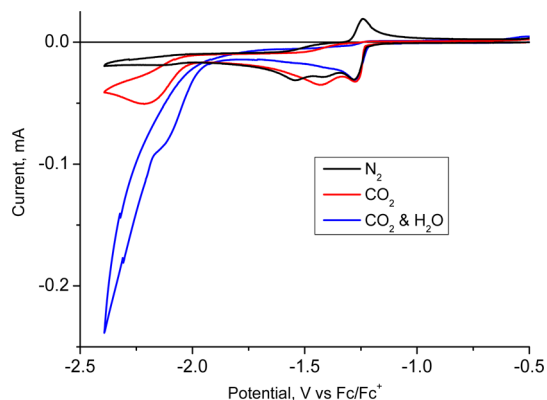


Figure 4. Cyclic voltammograms of 1 mM MnIMP in acetonitrile with 0.2 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ at a scan rate of 0.1 V s^{-1} , under an atmosphere of N_2 (black), CO_2 (red), and CO_2 with 4.7% H_2O (blue).

monosubstituted complexes **2** and **4**, a behavior indicative of a rapid reaction of the anion with CO_2 . A diminished but clear anodic wave of $[\text{Mn}(\text{CO})_3(\text{TBIEP})]^-$ can be observed under a CO_2 vs a N_2 atmosphere (Figure 3), suggesting that $[\text{Mn}(\text{CO})_3(\text{TBIEP})]^-$ associates with CO_2 less efficiently. While, similarly to MnIPIMP, no anodic wave corresponding to $[\text{Mn}(\text{CO})_3(\text{TBIMP})]^-$ reoxidation under a CO_2 atmosphere could be observed, indicating that CO_2 association is rapid, the overall current enhancement for this complex is comparatively low, indicating lower efficiency at reducing CO_2 , perhaps due to the bicarbonate intermediate somewhat preventing the recovery of the five-coordinate catalytic species.

Under N_2 , reduction of $[\text{MnBr}(\text{CO})_3(\text{IPIMP})]$ is seen at $E_{p,c} -1.49$ V, accompanied by a wave at $E_{p,c} -1.29$ V, assigned to the cationic aqua complex $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IPIMP})]^+$ (Figure 5). As discussed above, upon addition of CO_2 the oxidation wave of the anion $[\text{Mn}(\text{CO})_3(\text{IPIMP})]^-$ is not observed, indicating a rapid reaction between the five-coordinate anion

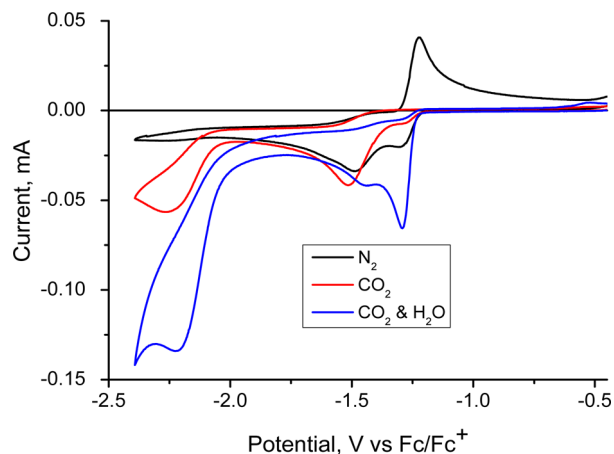


Figure 5. Cyclic voltammograms of 1 mM MnIPIMP in acetonitrile with 0.2 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ at a scan rate of 0.1 V s^{-1} , under an atmosphere of N_2 (black), CO_2 (red), and CO_2 with 4.7% H_2O (blue).

541 and CO₂. Some current enhancement at −2.26 V is observed
 542 upon saturation with CO₂, which is enhanced greatly upon the
 543 addition of 0.3 mL of water (the current enhancement
 544 corresponds to the cathodic wave of the bicarbonate complex,
 545 identified in the IR spectra (vide infra): some catalysis occurs
 546 due to hydrolysis caused for example by residual water in the
 547 electrolyte or in the CO₂).

548 CV of MnTBIMP (Figure 3, bottom panel) is similar to that
 549 of MnIPIMP and MnTBIEP with a strong cathodic wave at
 550 −1.45 V. At ca. −2.28 V current enhancements ascribed to CO₂
 551 reduction can be observed under CO₂ and CO₂ with added
 552 H₂O, though the $i_{\text{cat}}/i_{\text{p}}$ values (Table S11 in the Supporting
 553 Information) are somewhat lower in comparison to the other
 554 complexes studied here. Importantly, the anodic wave of the
 555 five-coordinate anion reoxidation is not detected for MnIPIMP
 556 and MnTBIMP but is clearly seen for slower reacting
 557 MnTBIEP and MnDIPIMP anions.

558 MnDIPIMP shows significant differences in the CV traces in
 559 comparison to the other complexes of the IMP subseries
 560 (Figure 6). Similarly to the IMP and IPIMP complexes, a

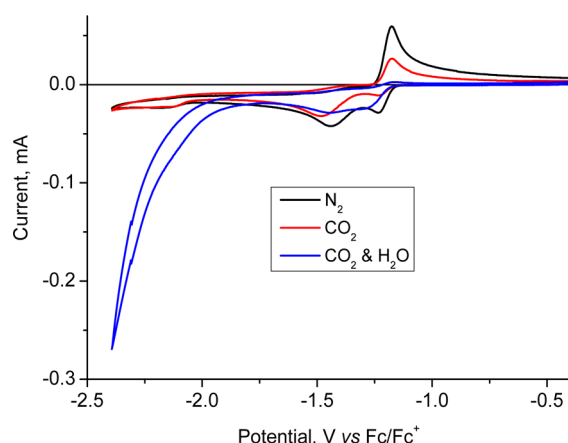


Figure 6. Cyclic voltammograms of 1 mM MnDIPIMP in acetonitrile with 0.2 M [Bu₄N][PF₆] at a scan rate of 0.1 V s^{−1}, under an atmosphere of N₂ (black), CO₂ (red), and CO₂ with 4.7% H₂O (blue).

561 formation of an aqua cation complex ([Mn(CO)₃(H₂O)-
 562 (DIPIMP)]⁺) is observed in solution. However, upon
 563 saturation with CO₂ no additional processes (intermediate
 564 bicarbonate complex reduction) or current enhancement below
 565 −2 V is observed and the anodic peak due to oxidation of
 566 [Mn(CO)₃(DIPIMP)][−] does not fully disappear. This suggests
 567 that the reduced complex is less prone to interact with CO₂, as
 568 would be expected due to the increased steric hindrance and
 569 structural rigidity of the complex arising from the two ⁱPr
 570 substituents at the N-phenyl rings.

571 **IR and UV–Vis Spectroelectrochemistry under an
 572 Inert Atmosphere.** IR spectroscopy²⁰ is an ideal tool to
 573 monitor the cathodic processes in the studied complexes, due
 574 to presence of the carbonyl ligands as strong IR reporters.
 575 Table 2 gives the key experimental and calculated vibrational
 576 frequencies for the starting complexes and several relevant
 577 intermediate and dimer species. IR spectroelectrochemistry
 578 (IR-SEC) was used to probe the intermediates produced upon
 579 reduction and to monitor their presence during CO₂ reduction.

580 IR spectra of MnTBIEP (Figure 7) show, upon the first
 581 reduction, depletion of the parent $\nu(\text{CO})$ bands, with new
 582 bands growing in at 1922 and 1898 cm^{−1} and a broad feature at

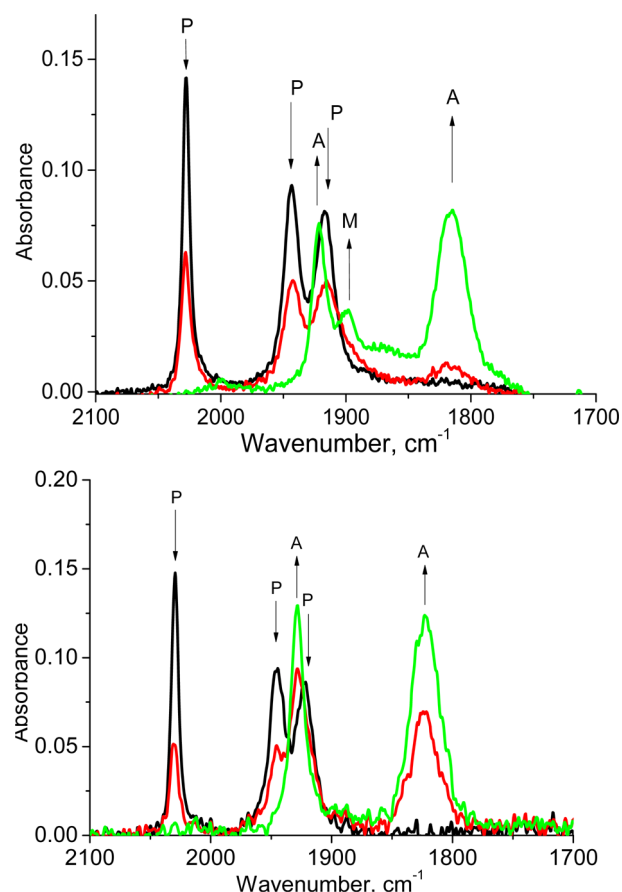


Figure 7. IR spectral changes accompanying in situ reduction of complexes in Ar-saturated acetonitrile/0.2 M [Bu₄N][PF₆] within an OTTE cell. (top) For MnTBIEP, a direct reduction of the parent complex (black line) to the five-coordinate anion (green line) is observed. : (P) [MnBr(CO)₃(TBIEP)]; (A) [Mn(CO)₃(TBIEP)][−]; (M) an unassigned side product. (bottom) For MnTBIMP, a direct reduction of the parent complex (black line) to the five-coordinate anion (green line) is observed: (P) [MnBr(CO)₃(TBIMP)]; (A) [Mn(CO)₃(TBIMP)][−].

1814 cm^{−1}. The bands at 1922 and 1814 cm^{−1} can be assigned
 to the five-coordinate anion [Mn(CO)₃(TBIEP)][−], an assign-
 ment supported by DFT calculations. The band at 1898 cm^{−1},
 which grows in after the five-coordinate anion begins to form,
 could tentatively be attributed to a decomposition product.
 UV–vis spectroelectrochemistry (Figure S113 in the Support-
 ing Information) supports this notion, as only a band at ca. 570
 nm has been detected, which corresponds to the five-
 coordinate anion. Differently from the MnIMP and MnIPIMP
 complexes (see below), there is no indication of dimer
 ([Mn(CO)₃(TBIEP)]₂) formation during the reduction of
 MnTBIEP on the time scale of the experiments performed.

MnTBIMP mirrors the behavior of MnTBIEP with the bands
 at 2029, 1945, and 1923 cm^{−1} corresponding to the parent
 complex being replaced concertedly with bands at 1928 and
 1823 cm^{−1} corresponding to the five-coordinate anion, with no
 intermediate species being observed. This would suggest that
 the direct formation of the five-coordinate anion is due to the
 steric demands of the ^tBu group, since the mono-ⁱPr derivative
 2 does exhibit dimer formation (Table 1).

The results of the IR-SEC study of MnIMP are shown in
 Figure 8. The first reduction of MnIMP in CH₃CN under an Ar
 atmosphere is accompanied by depletion of the parent IR bands

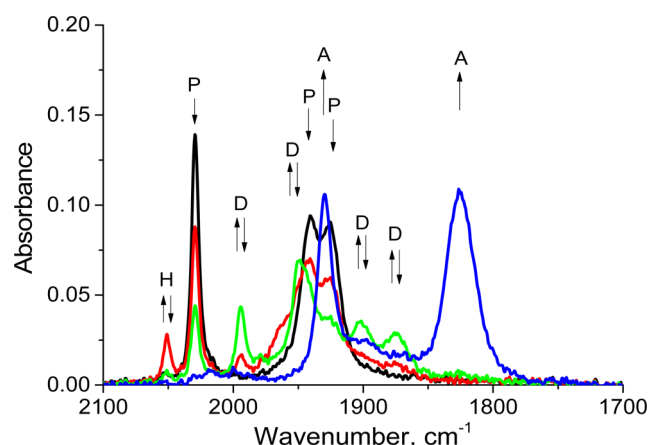


Figure 8. IR spectral changes accompanying in situ reduction of MnIMP in Ar-saturated acetonitrile/0.2 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ within an OTTLE cell. The parent complex $[\text{MnBr}(\text{CO})_3(\text{IMP})]$ (P, black line), and aquo cation $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IMP})]^+$ (H, additional features in the red spectrum) are reduced to the dimer $[\text{MnBr}(\text{CO})_3(\text{IMP})]_2$ (D, green line) followed by reduction of the dimer to the five-coordinate anion $[\text{Mn}(\text{CO})_3(\text{IMP})]^-$ (A, blue line). The intermediate spectrum (red line) recorded between those of the parent complex and the dimer also shows the features of the aquo complex.

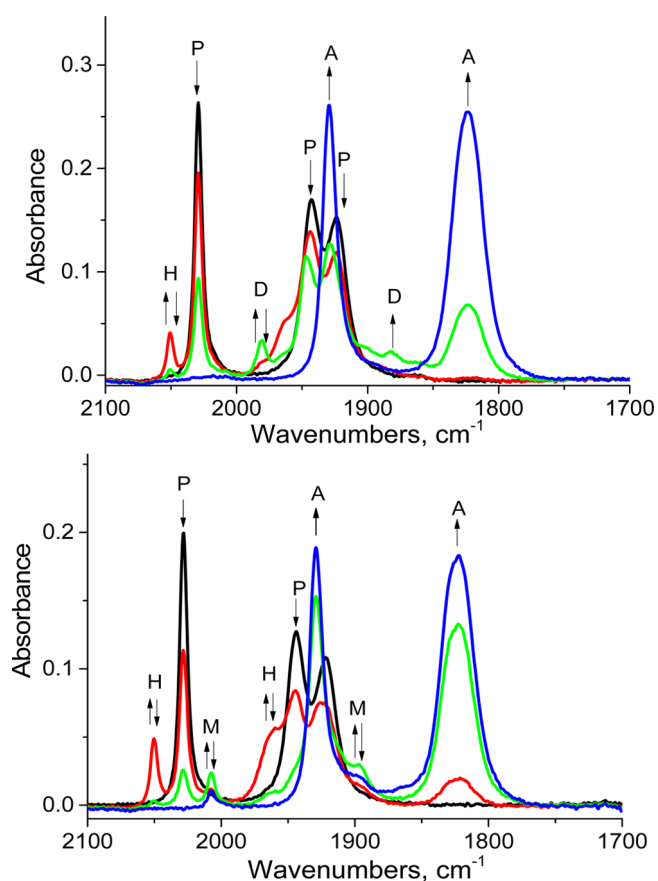


Figure 9. IR spectral changes accompanying in situ reduction of the complexes in Ar-saturated acetonitrile/0.2 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ within an OTTLE cell. (top) MnIPIMP, with concurrent formation of a dimer and a five-coordinate anion on reduction of the parent complex being observed: (P) $[\text{MnBr}(\text{CO})_3(\text{IPIMP})]$; (D) $[\text{Mn}(\text{CO})_3(\text{IPIMP})]_2$; (A) $[\text{Mn}(\text{CO})_3(\text{IPIMP})]^-$; (H) $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IPIMP})]^+$. (bottom) MnDIPIMP, with reduction of the parent complex to a five-coordinate anion being observed: (P) $[\text{MnBr}(\text{CO})_3(\text{DIPIMP})]$; (A) $[\text{Mn}(\text{CO})_3(\text{DIPIMP})]^-$; (H) $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DIPIMP})]^+$; (M) $[\text{Mn}(\text{CO})_3(\text{MeCN})(\text{DIPIMP})]^\bullet$.

1823 cm^{-1} , assigned to the five-coordinate anion, grew in, followed closely by smaller peaks at 2007 and 1899 cm^{-1} . The second peak assigned to the five-coordinate anion at 1929 cm^{-1} was masked by the absorption of the parent complex at the beginning of the reduction process. We tentatively assign the peaks at 2007/1899 cm^{-1} to the solvent-coordinated radical species $[\text{Mn}(\text{CO})_3(\text{MeCN})(\text{DIPIMP})]^\bullet$, in analogy with $[\text{Re}(\text{CO})_3(\text{PrCN})(\text{Pr-PyCa})]^{17}$ (Pr-PyCa = (isopropylimino)-pyridine; PrCN = butyronitrile) which shows $\nu(\text{CO})$ bands at 2005 and 1885 (br) cm^{-1} . Further, since the anodic wave of the dimer oxidation is not observed in the CV of MnDIPIMP, but a 1e reduced radical species is observed in IR-SEC, it is evident that the DIPIMP ligand prevents dimerization.

MnTBIMP shows behavior intermediate to that of MnTBIEP and MnIPIMP: similarly to MnTBIEP, the $t\text{Bu}$ substituent prevents dimer formation upon reduction. However, differently from MnTBIEP, and similar to MnIPIMP, a rapid reaction with CO_2 takes place, which in the case of MnTBIEP is considerably slowed by the $\text{R} = \text{Me}$ group. It is important to note that if Mn–Mn dimer is reduced at the same or even less negative potentials than that of the parent complex, it will not be detected in the studies.⁹ Thus, the comments above

at 2029, 1941, and 1926 cm^{-1} . Simultaneously, the growth of new bands at 1994, 1949, 1902, and 1875 cm^{-1} is seen, which are characteristic of the Mn–Mn dimer $[\text{Mn}(\text{CO})_3(\text{IMP})]_2$. Additionally, a peak at 2051 cm^{-1} grows in initially, which is assigned to the intermediate aqua cation $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IMP})]^+$ observed also by cyclic voltammetry. Further reduction of the dimer leads to formation of broad absorption bands at 1826 and 1930 cm^{-1} , once the formation of the dimer species is complete. These features are characteristic of the formation of the five-coordinate anion $[\text{Mn}(\text{CO})_3(\text{IMP})]^-$. UV–vis spectroelectrochemistry performed in parallel with the IR-SEC experiment confirms the presence of both of these species (Figure SI14 in the Supporting Information) via the broad absorption band at ca. 800 nm (assigned to the dimer) and the intense absorption at ca. 675 nm (assigned to the five-coordinate anion).⁸ All complexes in the IMP subseries exhibited a small transient peak at ca. 2050 cm^{-1} upon reduction. This is assigned to the aquo complex $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{IMP})]^+$.

Differently from MnIMP, MnIPIMP showed concurrent formation of the dimer and the five-coordinate anion upon reduction of the parent complex (Figure 9, top). The introduction of the isopropyl substituent at the phenyl ring leads to the observation of a small amount of the five-coordinate anion $[\text{Mn}(\text{CO})_3(\text{IPIMP})]^-$ (absorbing at 1929 and 1824 cm^{-1}), which grows in alongside peaks indicative of dimer formation (1981, 1949, 1901, 1882, and 1862 cm^{-1}).

Importantly, the IR absorption bands, corresponding to both the dimer and the five-coordinate anion, grew in simultaneously. UV–vis spectroelectrochemistry confirmed the presence of both dimer and five-coordinate species in this case, as is evident from Figure SI13 in the Supporting Information).

In contrast, only the five-coordinate anion is detected already from the onset of the reduction of MnDIPIMP under the experimental conditions used. In this case, there is no evidence for the dimer formation during the reduction of the parent complex. As shown in Figure 9 (bottom), an intense peak at

regarding the absence of dimer formation only relate to the Br complexes studied here. Substituting Br[−] with a different group, which would lead to the parent complex being reduced at less negative potentials, may permit detection of these species. Five-coordinate complex formation appears to correlate with a less negative first reduction potential (see Table 3). A comparable

Table 3. Cathodic Potentials (V, vs Fc/Fc⁺) of the Parent Complexes [MnBr(CO)₃(IP)] (1 mM, Acetonitrile, 0.2 M [Bu₄N][PF₆]) and Corresponding Cationic Mn Aquo Derivatives Formed in Situ by Partial Hydrolysis

complex	<i>E</i> _{p,c}	catalytic potential ^b
[MnBr(CO) ₃ (IMP)] (1)	−1.41, −1.54 ^a	−2.21
[Mn(CO) ₃ (H ₂ O)(IMP)] ⁺	−1.28	
[MnBr(CO) ₃ (IPIMP)] (2)	−1.49	−2.26
[Mn(CO) ₃ (H ₂ O)(IPIMP)] ⁺	−1.29	
[MnBr(CO) ₃ (DIPIMP)] (3)	−1.44	−2.16
[Mn(CO) ₃ (H ₂ O)(DIPIMP)] ⁺	−1.23	
[MnBr(CO) ₃ (TBIMP)] (4)	−1.45	~−2.28
[MnBr(CO) ₃ (TBIEP)] (5)	−1.53	−2.18
[Mn(CO) ₃ (H ₂ O)(TBIEP)] ⁺	−1.35	

^aThis process probably corresponds to a reduction of the dimer.

^bLargely coinciding with the reduction of a bicarbonate complex (see the spectroelectrochemical section).

correlation was found for Mn-R-DAB complexes and sterically hindered 2,2'-bipyridines already reported in the literature. These complexes also exhibit less negative first reduction potentials in comparison to their less sterically hindered counterparts and form five-coordinate anions directly upon reduction.^{8,25}

IR and UV–Vis Spectroelectrochemistry under a CO₂ Atmosphere. Electrochemical behavior under a CO₂ atmosphere is vastly different from that under a N₂ or Ar atmosphere. The electrocatalytic reduction of CO₂ with the four Mn complexes can be described in terms of three different types of behavior, largely controlled by the steric hindrance of the active imino C=N bond. MnIMP and MnIPIMP are relatively unhindered, and the catalytic behaviors are almost identical. The initial reduction of parent and/or the cationic aqua complex results in the formation of the two-electron-reduced five-coordinate anion that reacts efficiently with CO₂; no dimer is observed during the reduction of MnIMP (Figure 10) or MnIPIMP (Figure 11).

The catalytic process at the initial cathodic wave is, however, inhibited by the rapid formation of a stable bicarbonate complex, absorbing at 2036, 1940, 1924, and 1671 cm^{−1} for the IPIMP species, in line with the reports for sterically hindered Mn-mesityl-bipyridine²⁵ complexes and Mn-R-DAB complexes.⁸ A further negative potential shift of ca. 0.7 V is needed to reduce the bicarbonate complex, resulting in the recovery of the five-coordinate anion that triggers the catalytic conversion of CO₂.

For the nonhindered IMP and IPIMP ligands the five-coordinate anion reacts rapidly and is not observed in the IR spectra on this time scale (for IMP) and only at a low concentration (for IPIMP). The production of CO in the thin solution layer results in the displacement of the α-diimine ligand in the five-coordinate anion, forming the pentacarbonyl species [Mn(CO)₅][−] clearly seen in the IR spectra via the growth of bands at 1897 and 1865 cm^{−1} (species C in Figures 10–13). Remarkably, in these two cases only a comparatively

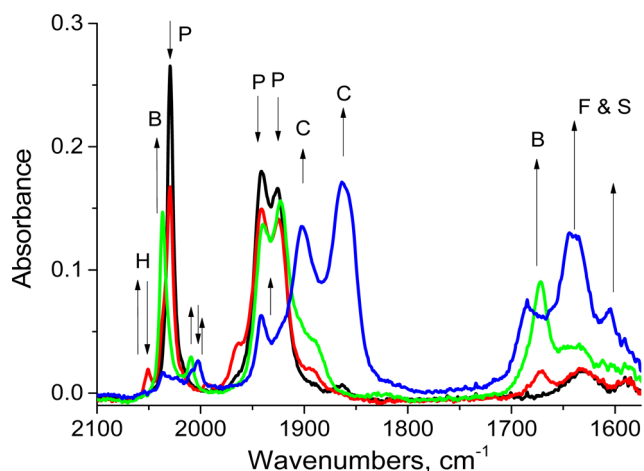


Figure 10. IR spectral changes accompanying in situ reduction of MnIMP ([MnBr(CO)₃(IMP)]) in CO₂-saturated acetonitrile/0.2 M [Bu₄N][PF₆] within an OTTE cell: (P) [MnBr(CO)₃(IMP)]; (B) [Mn(CO)₃(IMP)(η¹-OCO₂H)][−]; (C) [Mn(CO)₅][−]; (H) [Mn(CO)₃(H₂O)(IMP)]⁺; (F and S) free bicarbonate (OCO₂H[−]) and subordinate formate (OCHO[−]) accompanying the catalytic reduction of CO₂ to CO.

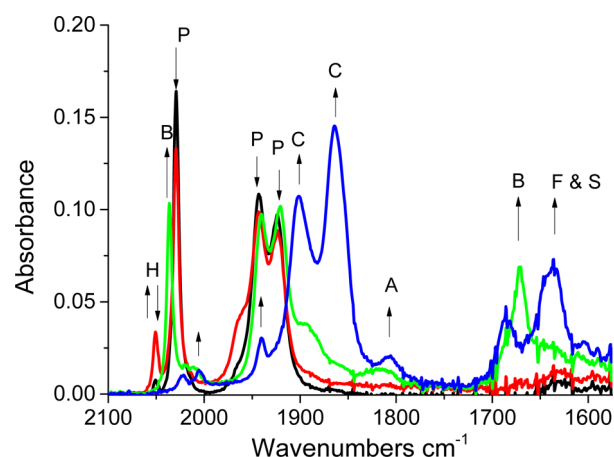


Figure 11. IR spectral changes accompanying in situ reduction of MnIPIMP ([MnBr(CO)₃(IPIMP)]) in CO₂-saturated acetonitrile/0.2 M [Bu₄N][PF₆] in an OTTE cell: (P) [MnBr(CO)₃(IPIMP)]; (A) [Mn(CO)₃(IPIMP)][−]; (B) [Mn(CO)₃(IPIMP)(η¹-OCO₂H)][−]; (C) [Mn(CO)₅][−]; (H) [Mn(CO)₃(H₂O)(IPIMP)]⁺; (F and S) free bicarbonate (OCO₂H[−]) and subordinate formate (OCHO[−]) accompanying the catalytic reduction of CO₂ to CO.

small amount of free bicarbonate or free formate (1685, 1638, and 1604 cm^{−1} for the IPIMP species) relative to [Mn(CO)₅][−] is observed, marking the high catalytic efficiency toward CO production.

Upon reduction of the more C=N hindered DIPIMP complex, the five-coordinate anion formed does not react with CO₂ efficiently and a metastable population of the anionic five-coordinate MnDIPIMP species [Mn(CO)₃(DIPIMP)][−] is detected even under a high excess of CO₂. Interestingly, and differently from the other complexes in the Mn-IP series, the formation of a bicarbonate complex is only detected at the potential corresponding to the reduction of CO₂-associated species at around −2 V vs Fc/Fc⁺, while on prior coordination of CO₂ to the five-coordinate anion at the parent MnDIPIMP cathodic wave no bicarbonate ligand signature is detected. At the catalytic potential where the bicarbonate complex is

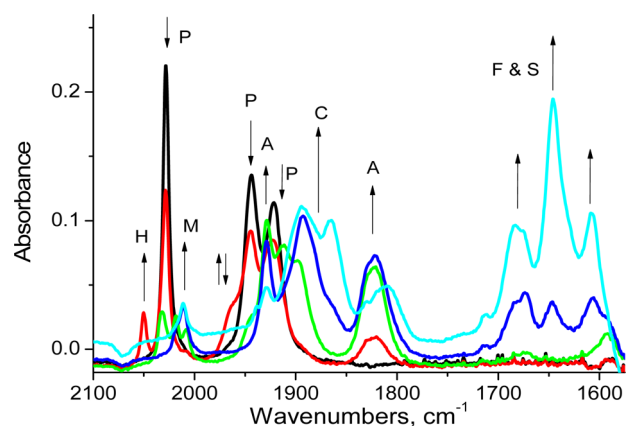


Figure 12. IR spectral changes accompanying in situ reduction of MnDIPIMP in CO₂-saturated acetonitrile/0.2 M [Bu₄N][PF₆] within an OTTLE cell: (P) [MnBr(CO)₃(DIPIMP)]; (A) [Mn(CO)₃(DIPIMP)][−]; (B) [Mn(CO)₃(DIPIMP)(η¹-OCO₂H)]; (H) aqua complex [Mn(CO)₃(H₂O)(DIPIMP)]⁺; (C) [Mn(CO)₅][−]; (M) [Mn(CO)₃(MeCN)(DIPIMP)]⁺; (F and S) free bicarbonate (OCO₂H[−]) and subordinate formate (OCHO[−]).

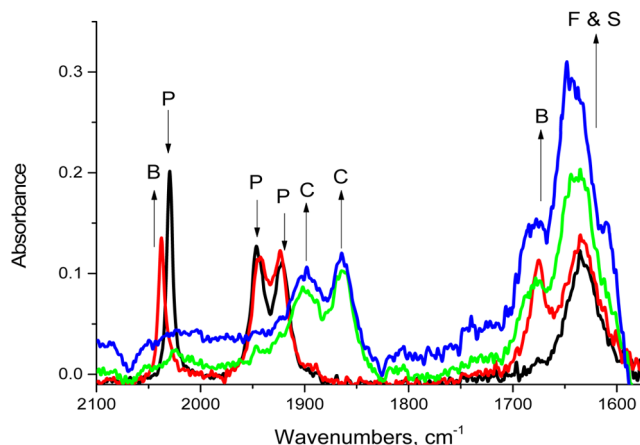
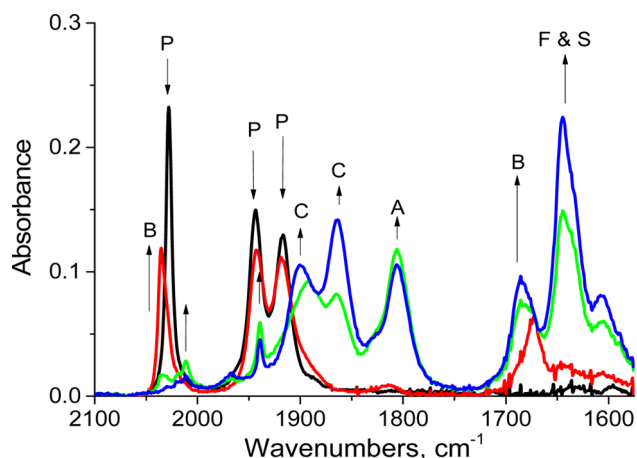


Figure 13. IR spectral changes accompanying in situ reduction of complexes in CO₂-saturated acetonitrile/0.2 M [Bu₄N][PF₆] within an OTTLE cell. (top) For MnTBIEP: (P) [MnBr(CO)₃(TBIEP)]; (A) [Mn(CO)₃(TBIEP)][−]; (B) [Mn(CO)₃(TBIEP)(η¹-OCO₂H)]; (C) [Mn(CO)₅][−]; (F and S) free bicarbonate (OCO₂H[−]) and formate (OCHO[−]) accompanying the catalytic reduction of CO₂ to CO. (bottom) For MnTBIMP: (P) [MnBr(CO)₃(TBIMP)]; (B) [Mn(CO)₃(TBIMP)(η¹-OCO₂H)]; (C) [Mn(CO)₅][−]; (F and S) free bicarbonate (OCO₂H[−]) and formate (OCHO[−]) accompanying the catalytic reduction of CO₂ to CO.

reduced, the conversion of CO₂ to CO is also inefficient. A high concentration of the five-coordinate anion is still seen, converting slowly to [Mn(CO)₅][−] when the concentration of CO increases; at the same time the production of free bicarbonate (and free formate) is much higher in comparison to the MnIMP and MnPIIMP cases, marking the low catalytic efficiency toward CO production. Notably, the lower CO-stretching band of [Mn(CO)₃(DIPIMP)][−] becomes shifted from its standard position (1829/1822 cm^{−1}) to lower energy (ca. 1810 cm^{−1}) at the advanced stage of the catalytic conversion. This shift may indicate the presence of an observable adduct of the five-coordinate anion, most likely with CO₂ or formate (over the Mn–N=C bond). In this context it is interesting to note that the related Re-IP complex³⁷ forms the carbonate complex in two 1e-reduction steps, via a direct coordination to the Re center, without C=N being directly involved.

In the case of MnTBIEP the imino C=N bond is hindered both at the carbon atom via the methyl group and by the *tert*-butyl group on the phenyl moiety. There are similarities with but also differences from the hindered DIPIMP complex, which does not have a hindering group at the C atom of the imino C=N moiety. Upon reduction of the parent complex in CO₂-saturated acetonitrile the five-coordinate anion [Mn(CO)₃(TBIEP)][−] coordinates CO₂, forming the bicarbonate complex readily (similar to IMP and IPIMP) with the characteristic IR absorption band at 1673 cm^{−1}.^{8,30} A small amount of the five-coordinate anion [Mn(CO)₃(TBIEP)][−] is observed in the initial step. Lowering the potential to around −1.5 V vs Fc/Fc⁺ results in catalytic conversion of the bicarbonate complex; however, similar to MnDIPIMP this conversion is not efficient in comparison with MnIMP and MnPIIMP. This is shown via the slower growth of [Mn(CO)₅][−] in comparison to IPIMP and the greater quantities of free bicarbonate produced. As with MnDIPIMP the five-coordinate anion “adduct” form is observed with the lower energy CO-stretching band shifted to a lower wavenumber (from 1814 to 1803 cm^{−1}). Thus, hindering the imine C atom does not affect adduct formation between CO₂ and [Mn(CO)₃(TBIEP)][−].

However, at the negative potentials where the bicarbonate complex is reduced (recovering the catalytic five-coordinate anion) the hindrance provided by the methyl and *tert*-butyl groups also negatively affects the catalytic formation of CO₂ to CO (as evidenced by large amounts of free bicarbonate and slow formation of [Mn(CO)₅][−] at lower CO concentration). It is not very clear whether this greater hindrance is due directly to the presence of the methyl group on the C position or whether this is due to the *tert*-butyl group inhibiting rotation of the phenyl moiety and preventing the five-coordinate anion from adopting a more suitable (pyramidal) geometry for CO₂ association.

Again, MnTBIMP behaves in a fashion similar to that of MnTBIEP. Upon reduction the parent complex rapidly associates CO₂, forming the bicarbonate complex; as the reduction potential is lowered further, the bicarbonate complex is reduced, forming CO which is able to displace the TBIMP and forming [Mn(CO)₅][−]. One important difference is that significantly less (if any) five-coordinate anion is observed in the presence of CO₂ than was the case with both MnTBIEP

785 and MnDIPIMP. This suggests that ^tBu is not as sterically
786 demanding as two ⁱPr groups in these systems, as CO₂ is still
787 able to coordinate.

788 **Estimation of Electrocatalytic Activity toward CO**
789 **Production using Gas Chromatography.** The CO
790 concentration as a function of time in the course of controlled
791 potential electrolysis estimated by GC analysis of the headspace
792 of the electrolysis cell shows a gradual buildup of CO in the
793 course of the electrolysis (Figure SI19 in the Supporting
794 Information). A comparison with the performance of [MnBr-
795 (CO)₃(bpy)] catalyst investigated under identical conditions
796 (see Figure S19) shows that the efficiency of CO production
797 for the new catalysts 1–5 is comparable to that of
798 [MnBr(CO)₃(bpy)], with the least sterically hindered
799 MnIMP complex being somewhat more efficient. Due to the
800 large volumes used in the experiment, considerable secondary
801 processes occur during bulk electrolysis, manifested in the loss
802 of the initial intense yellow-red color of the solution as the
803 reaction progressed, which was concomitant with an increase in
804 current toward the end of the electrolysis. These deviations
805 from an ideal behavior suggest that, as CO₂ is depleted in
806 solution, competing catalyst degradation pathways begin to
807 occur, precluding reliable estimates of efficiencies.

808 Estimation of efficiency from the CV data was done by the
809 relative $i_{\text{cat}}/i_{\text{p}}$ values (Table S1 in the Supporting Information)
810 following the method described in refs 4 and 7. Comparing the
811 current values detected in the CV at −2.24 V (vs Fc/Fc⁺)
812 recorded under a CO₂ and N₂ atmosphere in acetonitrile/water
813 also shows that the performances of 1–5 are comparable to one
814 another and are comparable to that of [Mn(CO)₃(bpy)Br], at
815 30–60% efficiency. It is important that the most sterically
816 protected complexes, MnDIPIMP and MnTBIEP, seem to be
817 performing better as far as $i_{\text{cat}}/i_{\text{p}}$ values are concerned but that
818 the least sterically hindered complex, MnIMP, is the most
819 efficient in the series. These observations are different from the
820 observation of MnTBIMP producing more CO than [Mn-
821 (bpy)(CO)₃Br] in the bulk electrolysis/GC experiments. While
822 these data can only be considered in relative terms, they do
823 show the potential of these complexes to act as a test bed for
824 optimizing steric vs electronic effects in CO₂ reduction,
825 whereby the thermodynamic factors, the rate of CO₂
826 coordination, and the rate of decomposition of catalyst
827 precursor species need to be balanced.

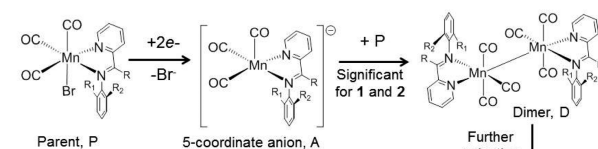
828 The main transformation pathways of 1–5 upon reduction
829 under an inert atmosphere, and under an atmosphere of CO₂,
830 are summarized schematically in Figure 14.

831 CONCLUSIONS

832 A series of Mn(I) tricarbonyl electrocatalysts for CO₂ reduction
833 which employ, for the first time, asymmetric α -diimine ligands,
834 imino-pyridines, has been developed, and their catalytic activity
835 has been confirmed and evaluated in detail.

836 We have demonstrated through conventional and thin-layer
837 cyclic voltammetry, UV–vis and IR spectroscop, and DFT
838 computational analysis the π decoupling of the phenyl from the
839 Mn(pyridine-CCN) metallacycle. The practical effect of this
840 feature is the ability to disentangle steric and electronic effects
841 of the α -diimine ligand on the catalytic properties. Until now,
842 introduction of sterically bulky groups, which are also typically
843 electron donating, was coming at the price of an increased
844 overpotential required for CO₂ reduction. The use of an
845 asymmetric α -diimine has allowed us to probe the effect of
846 adding ever greater sterically demanding groups without much

(a) inert atmosphere



(b) CO₂ atmosphere

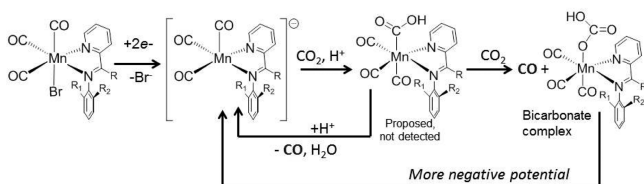


Figure 14. Main transformation pathways of 1–5 upon reduction under (a) an inert atmosphere and (b) an atmosphere of CO₂. A is detected for 3 only due to the comparatively slower reaction of [3][−] with CO₂.

change in the catalytic potential. We have demonstrated that a
systematic increase in the steric hindrance of the R₁ and R₂
groups in the IMP subseries results in the switch of the nature
of the first reduction product detected on the time scale of the
experiment under an inert gas atmosphere, from a dimer to a
five-coordinate anion, at a very similar reduction potential. In
the absence of sterically hindering groups on the phenyl ring,
MnIMP, a dimer is formed, while increasing the steric
hindrance by adding ^tPr groups to the R₁ and R₂ positions
(MnDIPIMP) resulted in direct formation of the five-
coordinate anion, in line with prior observations for similar
sterically hindered ligands.^{23,26} MnIPIMP (in which case the
dimer may be reduced at the parent cathodic wave due to
slightly negatively shifted reduction potential vs that for
MnIMP) exhibited behavior intermediate to that of MnIMP
and MnDIPIMP with both the dimer and the five-coordinate
anion observed to be formed concurrently. MnTBIMP and
MnTBIEP both formed the five-coordinate anion directly upon
reduction of the parent complex.

Under a CO₂ atmosphere, all of the complexes reduce CO₂
to CO. The buildup of CO in the thin-layer spectroelectro-
chemical cell resulted in the displacement of the α -diimine
ligand, forming [Mn(CO)₅][−]. The complex containing the
most sterically demanding ligand, DIPIMP, is as anticipated
least susceptible to α -diimine displacement with CO, forming
exclusively the five-coordinate anion upon the first reduction;
it also has the least propensity to coordinate CO₂, resulting in a
considerable buildup of the concentration of the five-coordinate
anion. An intermediate formation of the bicarbonate is also
likely, as a band at 1686 cm^{−1} is present at intermediate times.
Of particular interest is that the least sterically hindered
complex, MnIMP, seemed to form a CO₂-associated complex
directly upon the first reduction, with no significant formation
of the dimer being observed on the time scale of the
experiment. This behavior is similar to that reported for the
symmetric nonaromatic Mn-R-DAB (R = alkyl) compounds.^{8,30}
The formation of a stable bicarbonate complex, either through
the coordination to the metal center or via the imino C=N
bond,^{23,37} leads to the need for increased overpotential. From
that point of view, the steric hindering (protection) of the
metal center/the imino C=N bond in the Mn(IP) complexes
is advantageous, as it disfavors the Mn–Mn dimerization (when

MnIMP is compared with MnDIPIMP). However, such steric crowding also slows the catalytic conversion of CO₂ to CO at the negative overpotentials, as can be seen in the GC data and from the $i_{\text{cat}}/i_{\text{p}}$ values. A difference in the reactivity of MnTBIMP and MnTBIEP, where no dimer formation has been detected for either of the complexes in the IR-SEC experiments but where MnTBIEP exhibits slower CO₂ conversion due to R = CH₃, alters the HOMO–LUMO gap in comparison to the IMP series as well as introduces additional steric bulk, further supporting the notion that it is possible to separate steric and electronic factors to a large extent. Balancing these factors by careful ligand design may lead to the optimal solution.

The new family of CO₂ reduction catalysts presents an exciting platform for versatile and relatively independent tuning of steric and electronic properties, offering a far greater tunability in comparison to catalysts with aromatic bpy-based or nonaromatic R-DAB-based ligands and abundant options to refine and optimize Mn tricarbonyl CO₂ reduction catalysts.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01477.

Calculated frontier orbitals from HOMO-3 to LUMO+3 for all studied complexes, complete CV measurements, control experiments, crystallographic data, and ¹H NMR spectra of the new complexes (PDF)

Crystallographic data (CIF)

Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for F.H.: F.Hartl@reading.ac.uk.

*E-mail for J.A.W.: Julia.Weinstein@sheffield.ac.uk.

ORCID

Anthony J. H. M. Meijer: 0000-0003-4803-3488

Julia A. Weinstein: 0000-0001-6883-072X

Notes

The authors declare no competing financial interest.

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